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Insights into surface structure and performance of fluorinated silicates from cohesive energy studies

17 March 2016

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Integrity ★ Service ★ Excellence

Outline

- Background: Complexity of Fluorosilicate Interactions
- Performance comparisons of Fluorosilicate Compounds
- Surface Migration Studies of F-decyl-M2

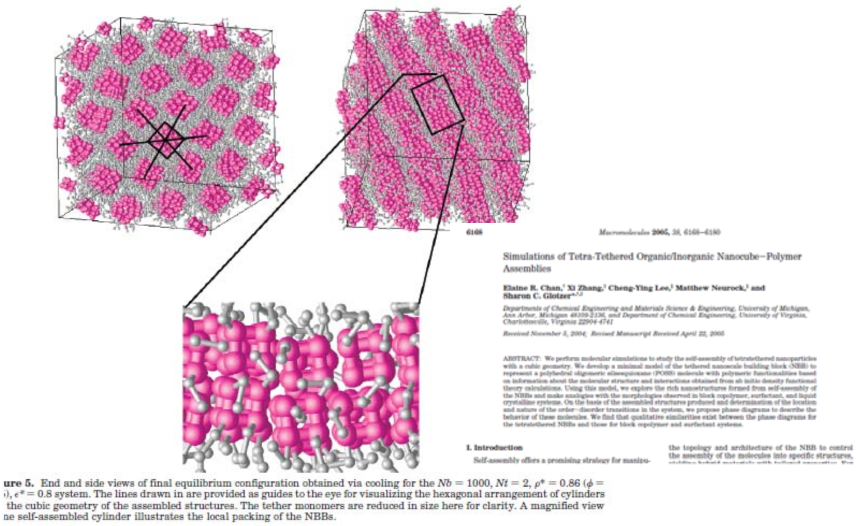
Acknowledgements: Air Force Office of Scientific Research, Air Force Research Laboratory, CSU STARS Program

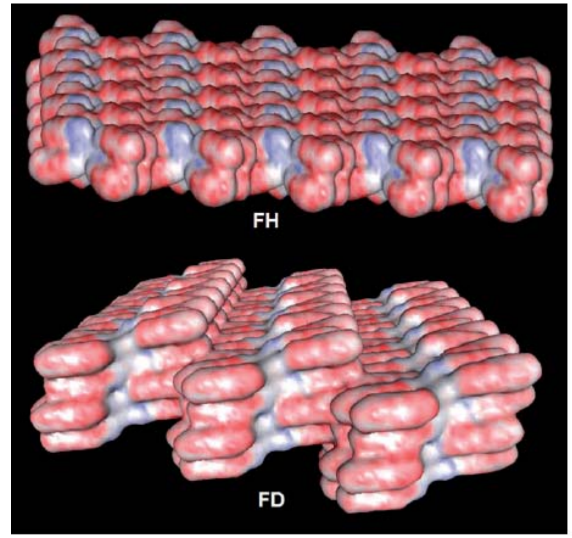
Why is Surface Science Essential for Propulsion?

- **Propulsion efficiency relies on achieving fast, controlled motion of fluids with minimal interference from solids**

Required: surfaces with well-controlled fluid interaction that can survive extreme environments → Si/O, F

Fluorosilicates Can Interact in Complex Ways





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- Translational Migration
- Phase Separation / Surface Concentration
- Self-Assembly
- Orentational Ordering (Intra-molecular and Inter-molecular)
- Peripheral Group Ordering (e.g. Intra-molecular Helices, Intermolecular Crystals)
- Molecular Ordering (e.g. Si – F Intra- and Inter-molecular Interaction, Cage-Cage Interactions)
- Dynamic Covalent Chemistry

Comparison of Surface Energy Parameters for Fluorosilicates

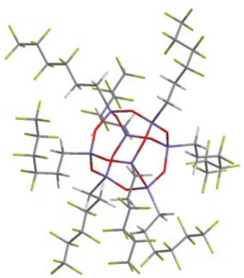
Table 3. Computed Values of the Dispersion (γ_{sv}^{d}), Acidic (γ_{sv}^{+}), and Basic (γ_{sv}^{-}) Components of Solid-Surface Energy (mN/m) for Various Fluoroalkylated Silicon-Containing Moieties

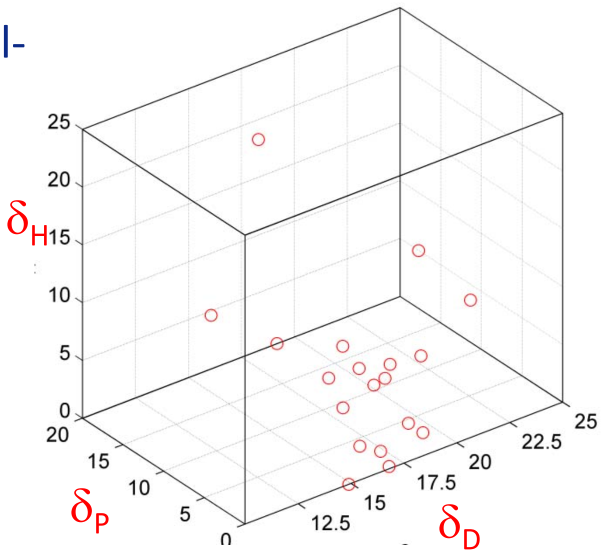
	alkanes (Zisman analysis)	all liquids[b] (eq 1 with $\varphi_{sl} = 1$)	diiodomethane, dimethyl sulfoxide and water (eq 5)				
	γ_c	γ_{sv}	γ_{sv}	dispersion (γ_{sv}^{d})	polar (γ_{sv}^{p})	acidic (γ_{sv}^{+})	basic (γ_{sv}^{-})
fluorodecyl T_8	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorooctyl T_8	7.4	10.6	10.9	10.6	0.3	0.2	0.1
fluorohexyl T_8	8.5	11.6	47.4	11.4	36.0	20.8	15.6
fluoropropyl T_8	19.7	18.7	38.4	19.1	19.3	11.8	7.9
hexafluoro-i-butyl T_8	17.7	19.1	26.9	26.8	0.1	0.002	0.8
fluorodecyl T_8	5.5	9.3	8.8	8.7	0.1	0.04	0.1
fluorodecyl Q_4	14.5	14.3	14.9	14.5	0.8	0.0	0.2
fluorodecyl M_2	19.6	26.8	39.7	30.9	8.8	2.0	9.7

- Typical Surface Energies: $-CF_3$ = 6 mN/m; $-CF_2-$ = 18 mJ/m; $-Si(CH_3)_2O-$ = 20 mJ/m; $-CH_2-$ = 27 mJ/m – depends on number density of groups
- F-decyl-T8 is typical of $–CF_3$, suggesting at least a highly oriented structure
- F-decyl-M2, despite having a similar make-up of group, is much higher, presumably due to random orientation (F-decyl-M2 in bulk is a liquid under ambient conditions)
- The values reported are also potentially affected by surface reorganization and solubility of the compounds in the probe liquids (F-decyl-T8 is highly insoluble, F-decyl-M2 is soluble in many liquids).

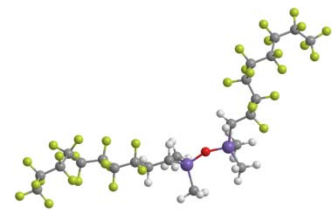
Cohesive Energy Characteristics of Fluorosilicates

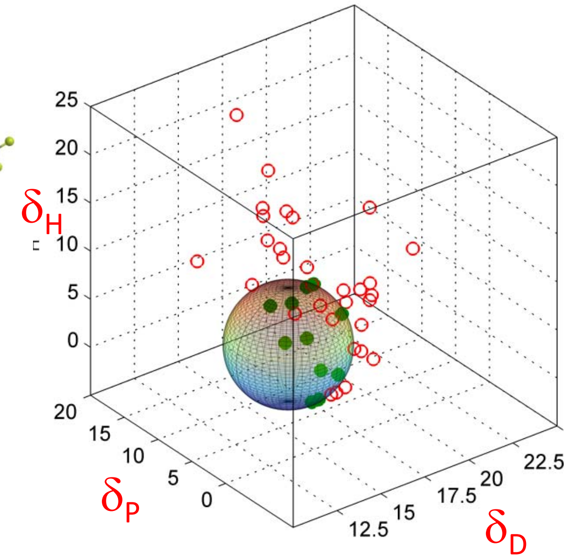
Octa-fluorohexyl-POSS





Fluorodecyl-M2



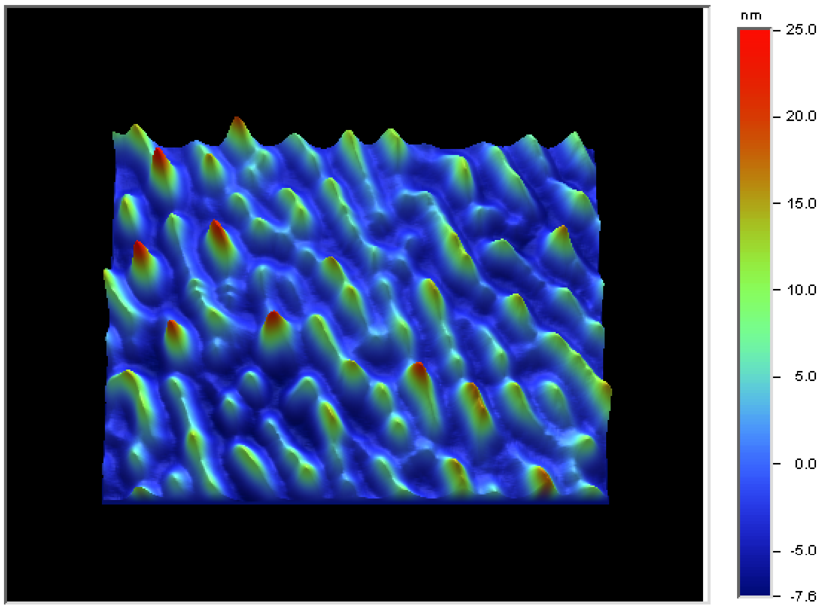


- Green dots indicate solubility > 100 mg/mL, red dots indicate solubility < 100 mg/mL
- Even the shorter-chain F-hexyl-T8 is highly insoluble compared to the F-decyl-M2

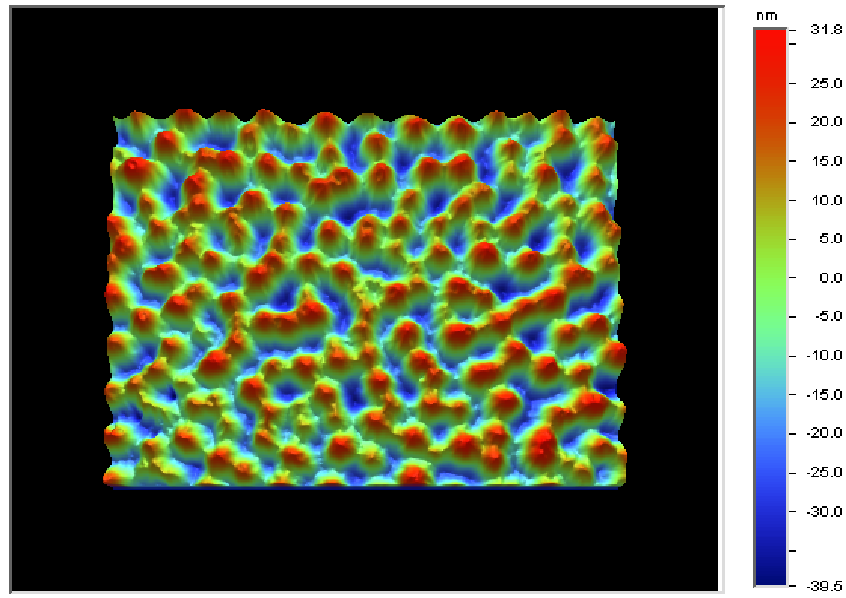
POSS / Silicate Type	δ_D	δ_P	δ_H	R_0	#Exceptions / #Good
Fluorodecyl-M2	15.0	4.3	4.0	6	0/11

Insolubility of F-decyl-T8 Drives Surface Migration / Crystallization

Domain Formation \from 20 Wt % Blend in PMMA, 10 mg/mL in AK225, Spin Coated @ 1500 rpm for 30 sec



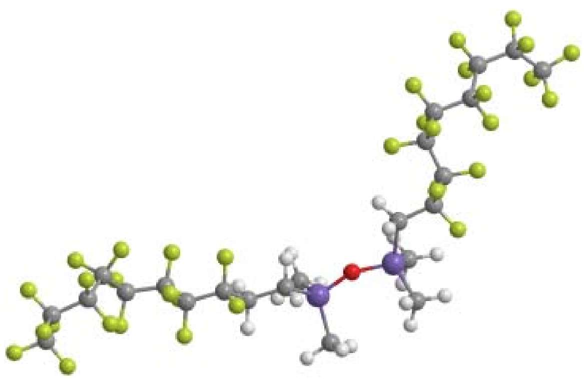
As-coated, R_a = 4 nm

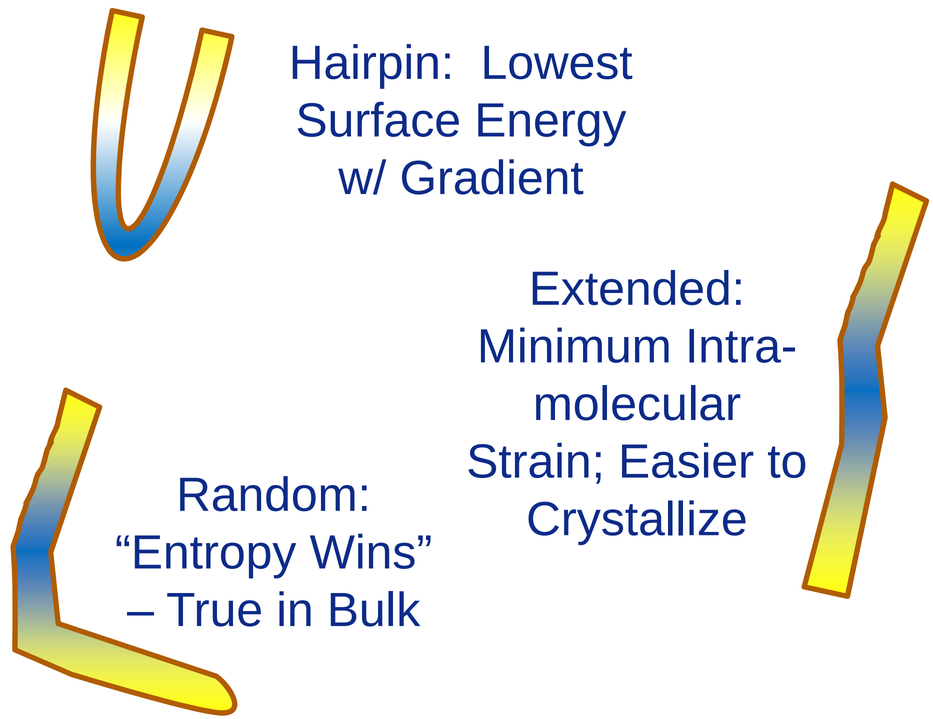


Annealed 110 °C, 270 min., R_a = 11 nm

F-decyl-T8 migrates to the surface and phase separates from matrices such as PMMA. Concentrated F-decyl-T8 at the surface crystallizes; the crystals create a surface texture. Surface energy, inhomogeneity, and texture each affect wetting properties..

F-Decyl-M2: Multiple Configurations Possible





The relatively high solubility of F-decyl-M2 enables potential competition among multiple driving forces during film formation when mixed with PMMA, cast, dried, and subsequently annealed.

Materials & Methods

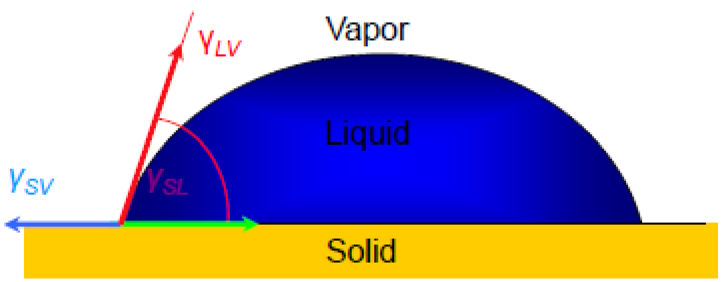
Matrix: 3 x 10^4 MW PMMA.

F-decyl-M2: synthesized at AFRL

Film Deposition: Achieved by dissolving both PMMA and F-decyl-M2 in dichloro-pentafluoropropane (AK225), 10 mg/mL total solids; 20-50 wt% F-decyl-M2, prepared via pin casting @ 1500 rpm for 30 sec Thermal annealing of films at temperatures of 80-110 C for 30 – 270 mins as an optional step

Analytical tools: direct observation (OM/SEM), surface deformation (interferometry), dynamic contact angle measurements

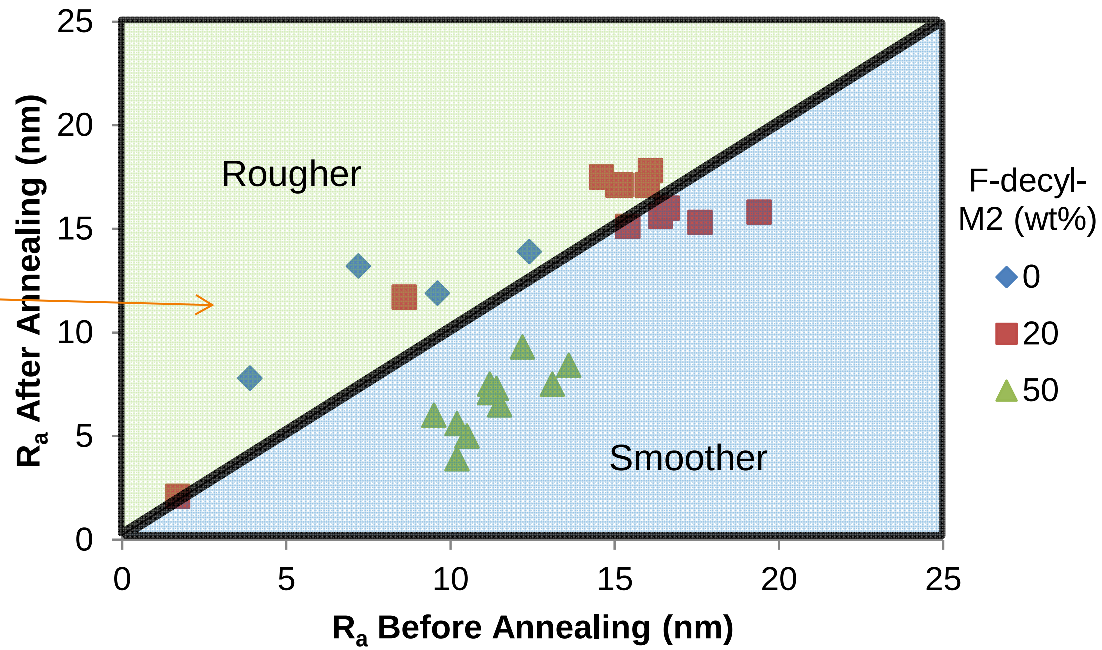
1. As-cast and equilibrium morphology
2. Dynamics of aggregate formation and growth
3. Aggregate morphology and its relationship to processing



F-decyl-M2 Acts as a Surface Plasticizer

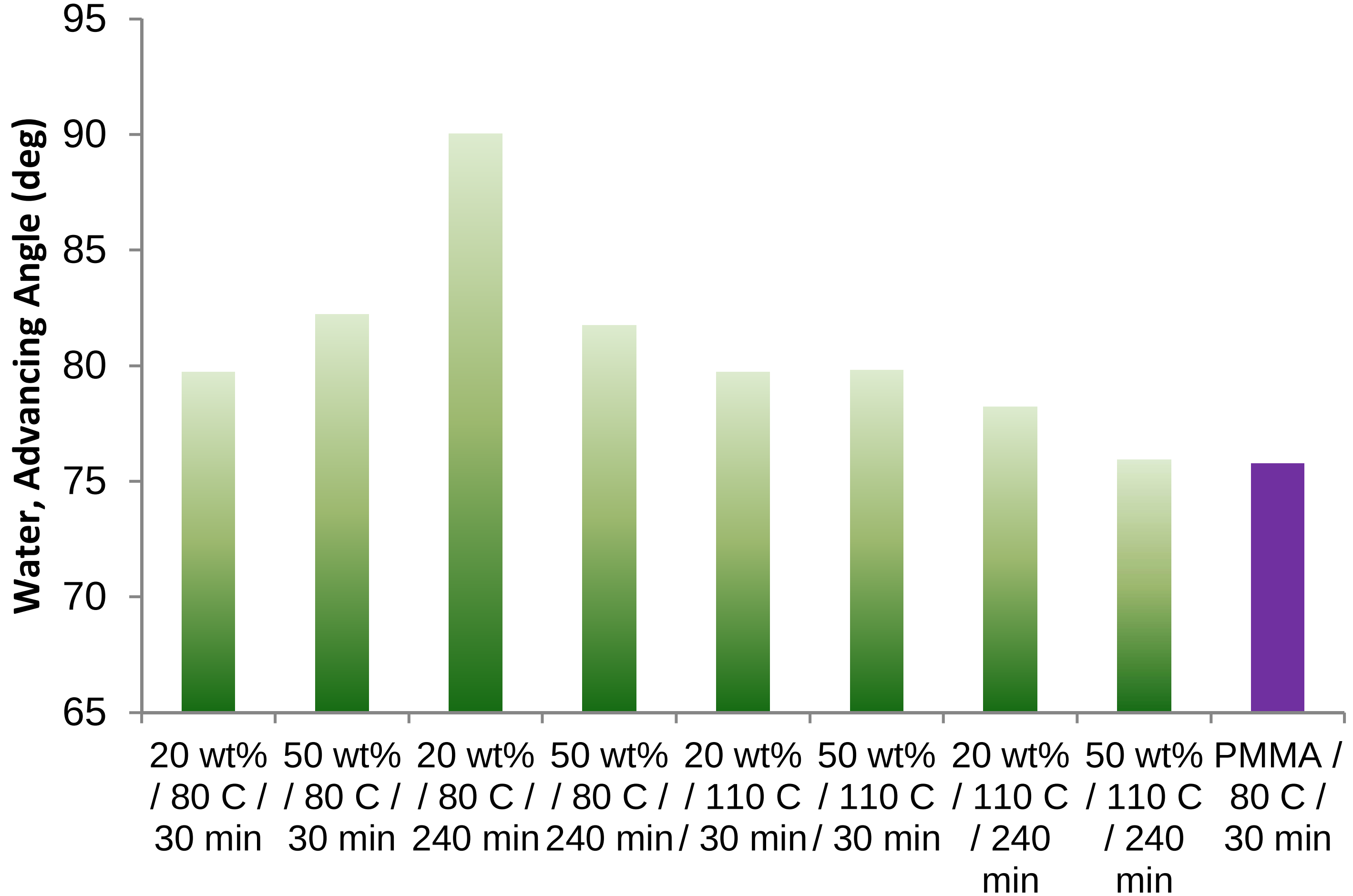
Comparison of Average Roughness Before and After Annealing (All Annealing Conditions)

20 wt%
F-decyl-T8



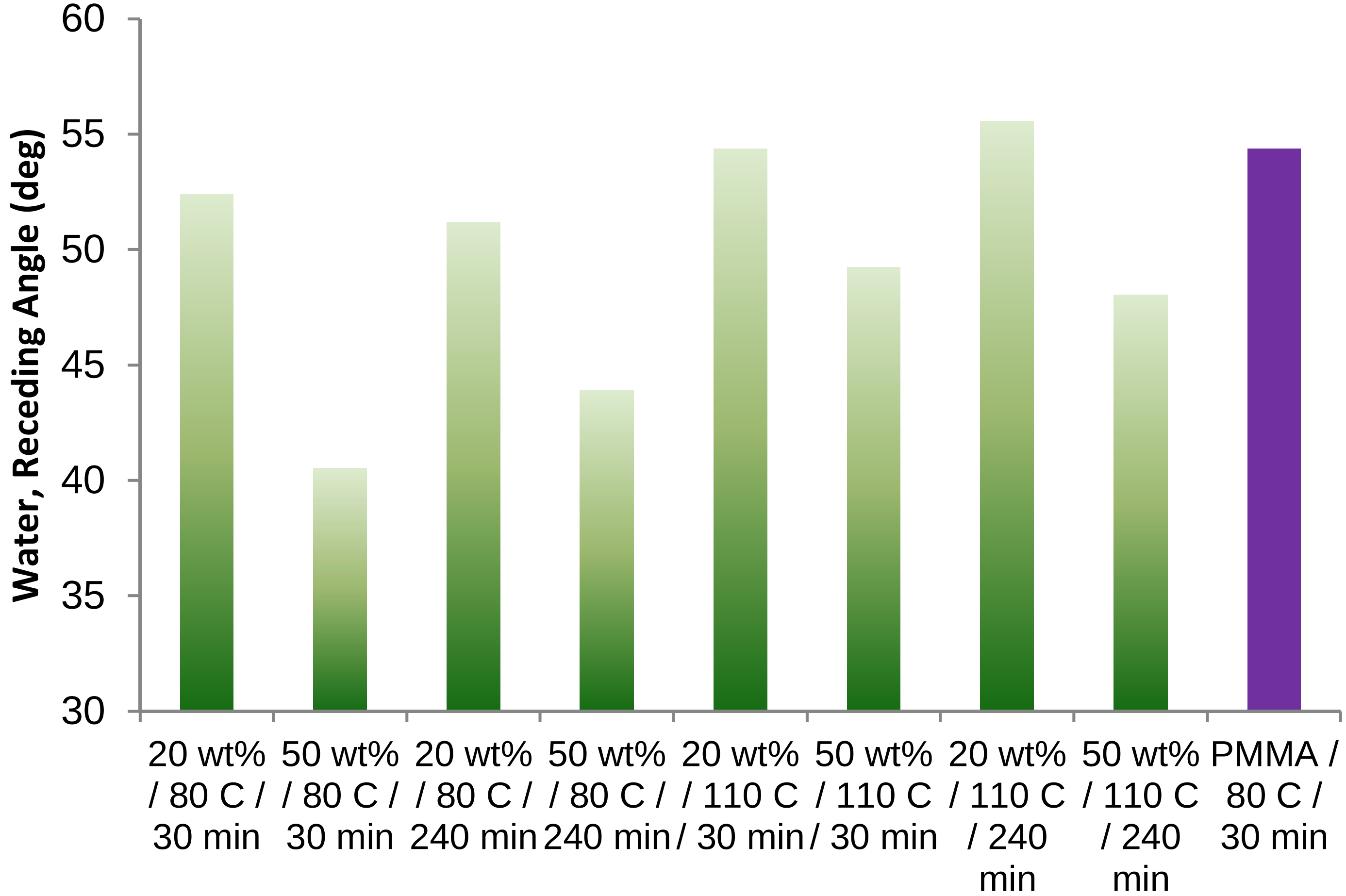
Spin casting produces “wrinkled” textures of ~10 nm average roughness; annealing slightly increases roughness in pure PMMA, but smooths it in mixtures rich in F-decyl-M2.

F-decyl-M2 / PMMA: Water Advancing Angles



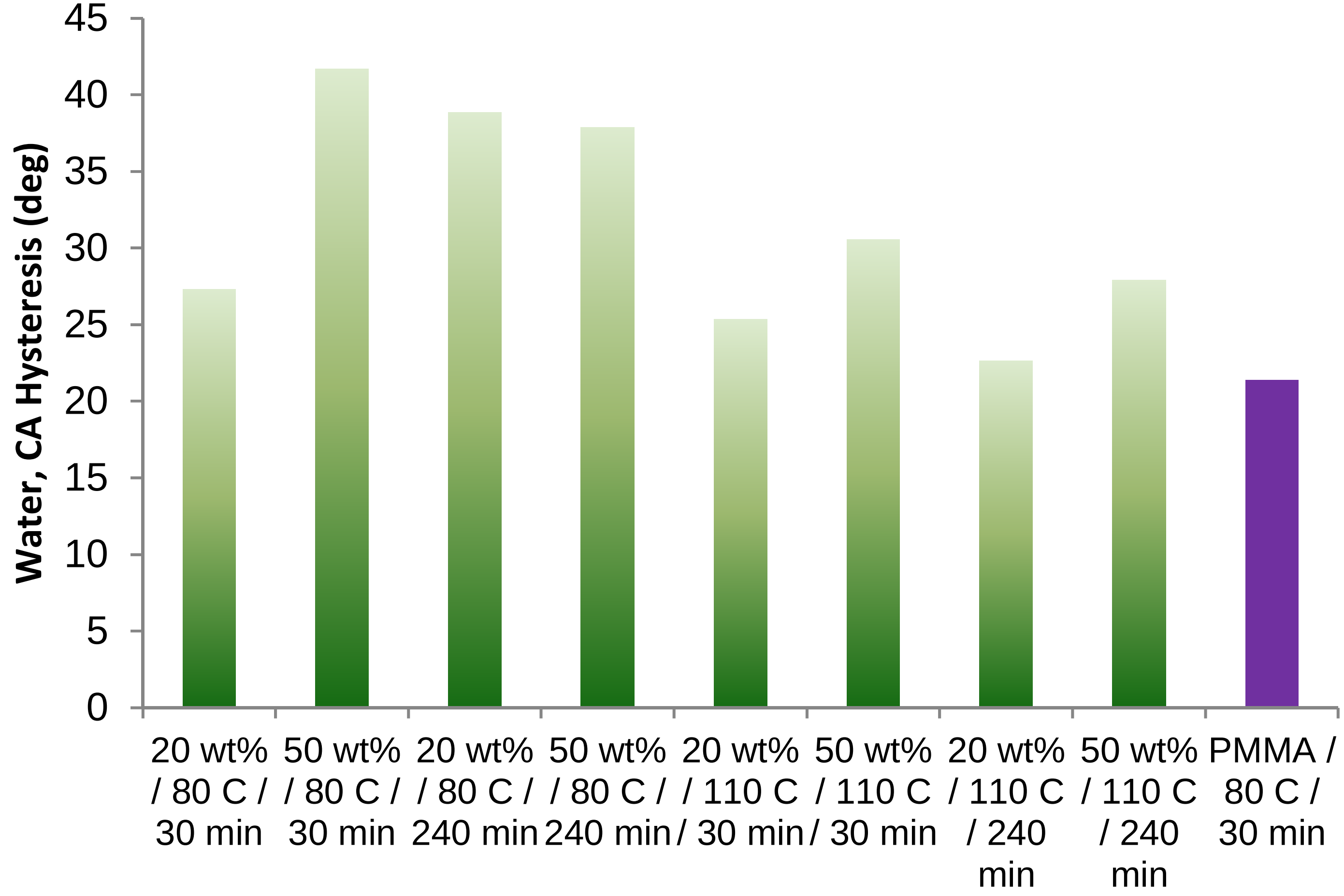
F-decyl-M2 surfaces tend to have slightly higher advancing contact angles compared to PMMA, in line with the slightly lower surface energy of F-decyl-M2

F-decyl-M2 / PMMA: Water Receding Angles



Definite trend toward lower receding angles at higher F-decyl-M2 loading; more extensive annealing tends to mitigate this effect

F-decyl-M2 / PMMA: Water CA Hysteresis



In general, lower F-decyl-M2 loading, and annealing above the matrix glass transition temperature, tends to result in lower hysteresis

Factors Responsible for CA Hysteresis in F-Decyl-M2 / PMMA

- **Roughness:** Samples tend to be wavy with ~50 nm amplitude and ~50 micron wavelength, therefore the Wenzel ratio is insignificantly different from unity. Thus, roughness should not contribute appreciably to hysteresis.
- **Heterogeneity:** Should result in both increased advancing angle coupled with decreased receding angle, does not seem to agree with data. Surface textures do not show evidence of significant heterogeneity development, though some may be present. Also does not explain hysteresis in pure PMMA. Nonetheless, needs to be checked via XPS / EDAX.
- **Rearrangement:** Should result in little change in advancing angles with large change in receding angle. Expected to be more significant with higher F-decyl-M2 loading, and the most "molecularly random" (least annealed) samples. Consistent with data.

Summary

- Spin coated films of F-decyl-M2 / PMMA are smooth enough to avoid too much interference with contact angle measurements from roughness, but are rough enough to probe relaxation effects on annealing
- F-decyl-M2 does appear to migrate to the surface, though the extent needs quantification
- The primary role of F-decyl-M2 appears to be as a plasticizer, meaning that no ordering is likely to take place; concentration of F-decyl-M2 at the air interface likely facilitates the random configurations typical of bulk material
- The plasticizing effect of F-decyl-M2 may facilitate rearrangement of the surface upon contact with water (likely bringing polar groups in PMMA to the surface); annealing may suppress this effect by allowing PMMA "trapped" near the surface during drying to move into the bulk.